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<b>(21) International Application Number:</b> PCT/GB94/01609 <b>(22) International Filing Date:</b> 27 July 1994 (27.07.94)  <b>(30) Priority Data:</b> 9317631.1                      25 August 1993 (25.08.93)                      GB  <b>(71) Applicant (for all designated States except US):</b> BXL PLASTICS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> DUGUID, Grant, William [GB/GB]; 9 Lombard Close, Barnsley, South Yorkshire S75 1AW (GB). GILL, Michael, Bert [GB/GB]; 25 Stillwell Drive, Sandal, Wakefield WF2 6RL (GB).  <b>(74) Agent:</b> KRISHNAN, Suryanarayana, Kalyana; BP International Limited, Patents & Agreements Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MULTI-LAYERED COMPOSITE  <b>(57) Abstract</b>  This invention relates to a multi-layer composite comprising one or more sequences comprising a base layer/tie-layer/EVOH/tie-layer/base layer, said composite having on at least one of its outer surfaces a conductive material either impregnated thereon or applied as a film on said outer surface. The base layer is preferably a polyolefin such as polyethylene. These composites are useful as vapour containment layers for fuel tanks.		

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MULTI-LAYERED COMPOSITE

This invention relates to a novel multi-layered composite comprising a plurality of polymer layers and a layer of a conducting material.

Composites comprising several polymers with or without a  
5 conducting layer are well known. In view of the limited ability of virgin polymeric layers to adhere to each other it is customary to introduce intervening tie layers having adhesive properties between the virgin polymers. Such tie layers may comprise grafting of maleic anhydride or acrylate ester polymers on to one surface of a  
10 polyolefin film and then applying thereon a further layer of a virgin polymer or a metallic layer in order to produce the desired composite. Such composites have found uses in various industries including the production of protective garments, canning of food products, and barrier films for oxygen, gasoline or other industries  
15 where toxic or hazardous emissions have to be contained. Such composites can also be used to produce a flexible vapour containment liner (hereafter "VCL") for a fuel tank system in order to minimise the risk of accidental ignition and to control emissions from such tanks whether eg they be used in automotive vehicles, aircraft or in  
20 oil tankers. However, in the composites used hitherto, the primary problem has been the inability of such composites when used as VCL to contain to the desired degree the emission of fuel vapours from such tanks.

It has now been found that by modifying the nature of and the  
25 components in the composites, an improved product can be produced

which has all the desirable properties including its ability to be used as a VCL thereby mitigating the problems of prior art composites.

Accordingly, the present invention is a multi-layer composite comprising one or more sequences comprising a base layer/tie-layer/EVOH/tie-layer/base layer, said composite having on at least one of its outer surfaces a conductive material either impregnated thereon or applied as an additional layer on said outer surface.

By the expression "composite" as used herein and throughout the specification is meant a product prepared either by lamination of several layers and/or by coextrusion of a number of components in order to give the desired product.

In the composite defined above, the expression "EVOH" signifies an ethylene-vinyl alcohol copolymer which may be derived by the hydrolysis of an ethylene-vinyl acetate copolymer.

In the composites of the present invention, the base layer may be that of a polyolefin, ethylene-vinyl acetate or an ionomer. The polyolefin layer, if used, may be suitably a layer of polyethylene, polypropylene or polybutene. Where the polyolefin layer is of polyethylene, it may be of high density polyethylene (hereafter "HDPE"), of low density polyethylene (hereafter "LDPE"), of linear low density polyethylene (hereafter "LLDPE") or very low density polyethylene (hereafter "VLDPE"). A layer of VLDPE is preferred. If the base layer is that of an ionomer, the ionomer is suitably a salt of (meth)acrylic acid. These are commonly available as the SURLYN® range of ionomers (ex Du Pont). Other ionomers which may be used in this invention include the commercially available IOTEK® (ex Exxon) range.

The thickness of each of the base layers in the composite is suitably in the range from 55-70µm, preferably from 60-65µm.

The tie-layer in the composite is the adhesive layer which binds the base layers, eg of polyolefin, with the layer of EVOH and/or the film of a conductive material. The tie-layer may be formed by grafting at least one polymerizable ethylenically unsaturated monomer (hereafter "EUM") which is suitably an

ethylenically unsaturated carboxylic acid, ester or anhydride on to a material which is the same as the base layer to form a graft-copolymer. This enables the tie layer to key in and blend into the base layer when preparing the composite. Thus, if the base layer is of polyethylene, it is preferable for the tie-layer to be a graft copolymer of polyethylene and a polymerizable ethylenically unsaturated monomer. Examples of such polymerizable ethylenically unsaturated monomers include maleic acid (hereafter "MA"), maleic anhydride (hereafter "MAH"), acrylic acid (hereafter "AA"), alkyl acrylate esters (hereafter "AAE"), methacrylic acid (hereafter "MAA"), alkyl methacrylate esters (hereafter "AME"), itaconic acid, citraconic acid, mesaconic acid, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo (2.2.2)oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3-dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro(4.4)non-7-ene, bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride (also known as and sold under the trade name NADIC ANHYDRIDE® by Allied Chemicals Corp and under HIMIC ANHYDRIDE® by Hitachi Chemical Co.), maleopimaric acid, tetrahydrophthalic anhydride, methyl-norborn-5-ene-2,3-dicarboxylic acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, and other fused ring monomers described in US-A-3 873 643 and US-A-3 882 194. Of these, maleic anhydride, tetrahydrophthalic anhydride and bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid anhydride are preferred.

Conjugated unsaturated esters, in addition to the alkyl acrylates and alkyl methacrylates mentioned above, may also suitably be used for cograftering. These esters include, eg, dialkyl maleates, dialkyl fumarates, dialkyl itaconates, dialkyl mesaconates, dialkyl citraconates, alkyl crotonates, alkyl tiglates wherein the alkyl group aliphatic, cycloaliphatic, alicyclic or an aralkyl group and suitably has 1-12 carbon atoms. Dibutyl maleate, diethyl fumarate and dimethyl itaconate are particularly preferred. These monomers may be used either alone or in combination with the anhydrides listed above and are suitably applied to at least one side of the base layer. Methods of grafting these monomers on to

the base layer are well known in the art. For instance, methods of grafting MAH to the base layer are described eg in US-A-2973344 and US-A-3290415. The grafting may be performed in a solvent by placing the monomer in a solvent followed by irradiation as

5 described in US-A-3290415 with peroxides. Alternatively, the grafting may be carried out, eg in the case of polypropylene, by melt mixing with peroxides. The peroxides that may be used include, eg, t-butyl hydroperoxide, p-menthane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide. Other grafting techniques  
10 include extrusion grafting and coating the polyolefin surface with a molten monomer followed by irradiation as described eg in US-A-3290415. These methods are incorporated herein by reference to these prior publications.

The thickness of the tie-layer is suitably from 1-5 $\mu$ m,  
15 preferably from 3-7 $\mu$ m. The material used for producing the tie-layer is suitably MAH.

The EVOH used is suitably of a grade which contains from 25-50 mol% of ethylene, preferably from 29-44 mol% and even more preferably from 32-38 mol %. Examples of EVOH grades that may be  
20 used include *inter alia*, the so-called EVAL® LCH 101 or EPJ 102B (both ex Kuraray Industries). The thickness of the EVOH layer is suitably from 7-20 $\mu$ m, preferably from 10-15 $\mu$ m.

The conductive material may be finely powdered carbon or metal which is present in an amount such that the conductivity of the  
25 impregnated layer is suitably from  $10^4$ - $10^5$  ohms per unit square. Powdered carbon is preferred due to its desired surface resistivity properties.

The conductive material may either be impregnated on the base layer or applied as a separate, additional layer on the base layer.  
30 Where this is applied as a separate layer, this separate layer is suitably that of a polyethylene or polyurethane containing powdered carbon or other metallic powder impregnated therein.

The co-extrusion, where used, is suitably carried out within an overall average temperature in the range from 210-230°C.,

35 Within this range the base layer is suitably maintained at 190-210°

C, and the EVOH layer at 210-220°C.

Where the composite is prepared by combining more than one sequence of base layer/tie-layer/EVOH/tie-layer/base layer, the adhesive used to combine such sequences is suitably a polyurethane adhesive. Examples of such adhesives that may be used include a polyester/polyurethane adhesive or a polyether/polyurethane adhesive. The adhesive can also be used to bind a layer of the conductive material to a base layer at one end of the composite. The composite preferably has at least two such sequences and the grades of any of the generic components in each sequence may be same or different.

The composites of the present invention and the use thereof as a VCL is illustrated with respect to the following Example:

EXAMPLE 1:

A specific example of the composite of the present invention is that comprising in sequence the following layers produced initially as 5-layer composites by co-extrusion of a EVOH (EPJ-102E, ex Kuraray) fed to be sandwiched between two layers of VLDPE (STAMYLEX® 09016, ex DSM) each of which VLDPE layers has an inner tie-layer of a copolymer of VLDPE grafted with MAH (ADMER® NF 520E, ex Kuraray) facing each other, using conventional techniques with a co-extruder (BARMAC four-component, 5-layer extruder) maintaining an average temperature of about 220°C. Two such composites having outer VLDPE facings were then laminated together using a two-component polyester/urethane adhesive ADCOTE®102A (which has a diisocyanate catalyst eg MDI or TDI, ex Morton International) to form an 11-layer composite in which the middle layer was the adhesive. This was followed by eventual lamination of one of the outer layers of the 11-layer composite with a carbon filled polyethylene resin grade B701A (ex British Polyethylene Industries Ltd) which forms the conductive layer. Thus, the final extended composite had the following structure:

VLDPE/TL/EVOH/TL/VLDPE/AD/VLDPE/TL/EVOH/TL/VLDPE/AD/CFP

wherein VLDPE represents - very low density polyethylene

TL represents - the graft copolymer of polyethylene

8 maleic anhydride used as tie-layer

EVOH represents - ethylene-vinyl alcohol

AD represents - the polyester/urethane adhesive

CFP represents - the carbon filled polyethylene

5 The extended composite so formed was cured at 40°C for 48 hours.

In such an extended composite the thickness ( $\mu\text{m}$ ) of the respective layers was as follows:

65/5/10/5/65/AD/62/5/15/5/63/AD/50

The adhesive layer, AD, was spread on the surface of the appropriate  
10 internal polyethylene layer in an amount of about  $5\text{g}/\text{m}^2$ .

The conductive layer of such an extended composite had a conductivity of  $1 \times 10^5$  ohms/unit<sup>2</sup>. The extended composite was subjected successfully to a flex test involving a repeated double folding of the extended composite over 2000 cycles without any  
15 change in its appearance or physical characteristics.

#### EXAMPLE 2:

The above process of Example 1 was repeated to produce a second composite except that in this case the EVOH layers were those of EVAL® LCH 101 (ex Kuraray). This extended composite was also  
20 subjected successfully to a flex test involving a repeated double folding thereof over 2000 cycles without any change in its appearance or physical characteristics.

#### EXAMPLE 3: TESTING AS VAPOUR CONTAINMENT LAYERS:

The extended composites from Examples 1 and 2, each of which  
25 had already been subjected to 2000 flexing cycles, were then used as a VCL for fuel tanks, the layer containing the conductive material being on the air side and the layer devoid of conducting material being on the fuel side of such a tank, to test its barrier properties. The volatile loss of fuel through the extended  
30 composites in each case, which had already been subjected to 2000 flexing cycles, was less than  $0.18\text{g}/24\text{hrs}/\text{m}^2$ .



## Claims:

1. A multi-layer composite comprising one or more sequences comprising a base layer/tie-layer/EVOH/tie-layer/base layer, said composite having on at least one of its outer surfaces a conductive material either impregnated thereon or applied as an additional layer on said outer surface.  
5
2. A composite according to Claim 1 wherein said composite is a product prepared either by lamination of several layers and/or by coextrusion of a number of components.
3. A composite according to any one of the preceding Claims wherein the base layer is that of a polyolefin, ethylene-vinyl acetate or an ionomer  
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4. A composite according to Claim 3 wherein the polyolefin base layer is a layer of polyethylene, polypropylene or polybutene.
5. A composite according to Claim 3 or 4 wherein the polyolefin  
15 base layer is of high density polyethylene, of low density polyethylene, of linear low density polyethylene or very low density polyethylene.
4. A composite according to Claim 3 wherein the base layer is that of an ionomer which is a salt of (meth)acrylic acid.
- 20 5. A composite according to any one of the preceding Claims wherein the thickness of each of the base layers is in the range from 55-70 $\mu$ m.
6. A composite according to any one of the preceding Claims wherein the tie-layer is the adhesive layer which binds the base  
25 layers with the layer of EVOH and/or the film of a conductive

material.

7. A composite according to any one of the preceding Claims wherein the tie-layer is formed by grafting at least one polymerizable ethylenically unsaturated monomer (hereafter "EUM") on to a material which is the same as the base layer to form a graft-copolymer.

8. A composite according to Claim 7 wherein the base layer is of polyethylene and the tie-layer is a graft copolymer of polyethylene and a polymerizable ethylenically unsaturated monomer.

9. A composite according to any one of the preceding Claims wherein the thickness of the tie-layer is from 1-5 $\mu$ m.

10. A composite according to any one of the preceding Claims wherein the EVOH is of a grade which contains from 25-50 mol% of ethylene.

11. A composite according to any one of the preceding Claims wherein the thickness of the EVOH layer is from 7-20 $\mu$ m.

12. A composite according to any one of the preceding Claims wherein the conductive material is finely powdered carbon or metal which is present in an amount such that the conductivity of the impregnated layer is from  $10^4$ - $10^5$  ohms per unit square.

13. A composite according to any one of the preceding Claims wherein the conductive material is either impregnated on the base layer or applied as a separate, additional layer on the base layer.

14. A composite according to any one of the preceding Claims wherein the composite is formed by a co-extrusion process operated within an overall average temperature in the range from 210-230°C and wherein the base layer is maintained at 190-210°C and the EVOH layer at 210-220°C.

15. A composite according to any one of the preceding Claims 1-13 wherein the composite is prepared by combining more than one sequence of base layer/tie-layer/EVOH/tie-layer/base layer and the adhesive used to combine such sequences is a polyurethane adhesive. Examples of such adhesives that may be used include a polyester/polyurethane adhesive or a polyether/polyurethane adhesive. The adhesive can also be used to bind a layer of the

conductive material to a base layer at one end of the composite.  
The composite preferably has at least two such sequences and the  
grades of any of the generic components in each sequence may be same  
or different.

5 16. A composite according any one of the preceding Claims wherein  
said composite is capable of being subjected to a flex test  
involving a repeated double folding thereof over 2000 cycles without  
any change in its appearance or physical characteristics.

10 17. A vapour containment layer comprising a composite according to  
any one of the preceding Claims for use in fuel tanks such that in  
use the layer containing the conductive material is on the air side  
and the layer devoid of conducting material is on the fuel side of  
such a tank.

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IPC 6 B32B27/08 F16L11/127

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 058 647 (INOUE ET AL.) 15 November 1977 see column 1, line 6 - line 37 see column 2, line 17 - line 18 see column 4, line 14 - line 29 see column 4, line 42 - line 46	1-17
Y	EP,A,0 470 606 (EMS-INVENTA AG.) 12 February 1992 see page 1, line 1 - page 2, line 3 see table 1, examples 5, 6 --- -/--	1-17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

Int:      nal Application No

PCT/GB 94/01609

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 365 266 (NIPPON PETROCHEM. CO., LTD.) 25 April 1990 see page 2, line 3 - line 8 see page 2, line 40 - line 46 see page 6, line 18 - line 20 see page 7, line 15 - line 24 see page 9, line 28 - line 30 -----	1-17

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